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(54) [Title of the invention]
Moisture resistant anti-reflection film
(Taishitsu hansha boshi maku)

(57) [Abstract]
[Purpose]
To offer an anti-reflection film that allows simple wiping of flow marking that is formed on a surface after evaporation of water droplets which are formed through exposure to a high humidity atmosphere.

[Constitution]
A moisture resistant anti-reflection film has characteristics as such that is composed through successful formation of the following layers on an optical glass substrate: first layer comprising SiO_2 showing 550 nm designed wavelength and 234 to 316 nm optical film thickness; second layer comprising HfO_2 or Ta_2O_5 showing 43 to 58 nm optical film thickness; third layer comprising SiO_2 showing 34 to 46 nm optical film thickness; fourth layer comprising HfO_2 or Ta_2O_5 showing 113 to 153 nm optical film thickness; fifth layer comprising SiO_2 showing 115 to 155 nm optical film thickness; and sixth layer comprising perfluoro alkyl silazane showing 5 to 15 nm optical film thickness.

(71) Applicant 000000527
Asahi Kogaku Kogyo Kabushiki Kaisha [Japanese company or Corporation]
36-9, 2-chome, Maeno-cho, Itabashi-ku, Tokyo

(72) Inventor
Hideo FUJII
c/o Asahi Kogaku Kogyo Kabushiki Kaisha
36-9, 2-chome, Maeno-cho, Itabashi-ku, Tokyo

Kiyoshi ARAKI
same as the above

(74) Agent
Kunio MIURA, patent agent

Amendments: There are no amendments to this patent.

[note: All names, addresses, company names, and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified with numeral prefix or general plurality suffix. translator's note]

[CLAIMS]
[Claim item 1]
A moisture resistant and anti-reflection film has characteristics as such that following layers are successfully formed on an optical glass substrate: first layer comprising SiO_2 showing 550 nm designed wavelength and 234 to 316 nm optical film thickness; second layer comprising HfO_2 or Ta_2O_5 showing 43 to 58 nm optical film thickness; third layer comprising SiO_2 showing 34 to 46 nm optical film thickness; fourth layer comprising HfO_2 or Ta_2O_5 showing 113 to 153 nm optical film thickness; fifth layer comprising SiO_2 showing 115 to 155 nm optical film thickness; and sixth layer comprising perfluoro alkyl silazane showing 5 to 15 nm optical film thickness.

[Claim item 2]
The moisture resistant and anti-reflection film according to the claim item 1, wherein alkyl group of perfluoro alkyl silazane is of alkyl group with 1 to 4 number of carbon atoms.

[DETAILED EXPLANATION OF THE INVENTION]
[0001]
[Fields of industrial application]
This invention relates to optical parts which constitute optical machinery and equipment; and in particular, it relates to an anti-reflection film suitable for optical parts which are used in an atmoshphere with high humidity.

[0002]
[Prior art and problem points]
As for the anti-reflection films which are generally used for optical parts such as lens or prism and the like which constitute optical machinery and equipment, for instance, an anti-reflection film that is prepared through successful formation of the following layers on a BK7 optical glass substrate (refractive index = 1.52) has been used: first layer comprising Al_2O_3 with 138 nm optical film thickness; second layer comprising ZrO_2 with 275 nm optical film thickness; and third layer comprising MgF_2 with 138 nm optical film thickness. However, according to this type of conventional anti-reflection film, in an atmosphere with high humidity that forms water droplets on its surface, when said water droplets evaporate over long hours, flow marking with white cloudy form remains where water droplets were present to present a problem point that it is not easy to remove this flow marking even when it is wiped with solvents such as alcohol and the like.

[0003]
[Purpose of this invention]
This invention's purpose is to solve above-explained problem points of the prior art, and to offer an anti-reflection film of which flow marking remaining after formation and evaporation of water droplets on a surface due to its exposure to an atmosphere with high humidity with a simple wipe off action.

[0004]
[Outline of this invention]
This invention attained above-explained purpose through a constitution of anti-reflection film of combination of HfO_2 or Ta_2O_5 that is a high refractive index material showing high moisture resistance, and SiO_2 that is a low refractive index material showing excellent moisture resistance in addition to forming of a layer comprising perfluoro alkyl silazane that is a water-repellent polymer material on its most outer layer.

[0005]
That is to say, this invention's moisture resistant and anti-reflection film has characteristics as such that following layers are successfully formed on an optical glass substrate: first layer comprising SiO_2 showing 550 nm designed wavelength and 234 to 316 nm optical film thickness; second layer comprising HfO_2 or Ta_2O_5 showing 43 to 58 nm optical film thickness; third layer comprising SiO_2 showing 34 to 46 nm optical film layer thickness; fourth layer comprising HfO_2 or Ta_2O_5 showing 113 to 153 nm optical film thickness; fifth layer comprising SiO_2 showing 115 to 155 nm optical film thickness; and sixth layer comprising perfluoro alkyl silazane showing 5 to 15 nm optical film thickness.

[0006]
According to this invention's anti-reflection film, as for the perfluoro alkyl silazane that constitutes said sixth layer, no particular restrictions are placed as long as it shows sufficient water repelling property as well as film forming property; however, the ones of which alkyl group has 1 to 4 number of carbon atoms are recommended. More concretely, perfluoro methyl silazane or perfluoro diethyl silazane and the like may be mentioned.

[0007]
As explained above, an anti-reflection film showing excellent moisture resistance is attained through forming an anti-reflection film comprising 5 layers of HfO_2 or Ta_2O_5 that is a high refractive index material showing high moisture resistance, and SiO_2 that is a low refractive index material showing excellent moisture resistance, and in addition, sixth layer comprising perfluoro alkyl silazane showing water repelling property so forming of water droplets is difficult on the surface of anti-reflection film even when it is exposed to an atmosphere with high humidity.

[0008]
Each layer that composes this invention's anti-reflection film may be formed through any optional methods such as vacuum vapor deposition method, sputtering method, ion plating method, or ion beam assist method and the like.

[0009]
[Examples]
This invention is further explained below in details with examples; however, this invention should not be limited with these examples.

[0010]
EXAMPLE 1
A BK7 optical glass substrate with 1.52 refractive index was heated to 250°C; and following layers were successfully formed on this through use of a vacuum vapor deposition device: first layer comprising SiO_2 showing 275 nm optical film thickness; second layer comprising HfO_2 showing 50 nm optical film thickness; third layer comprising SiO_2 showing 40 nm optical film thickness; fourth layer comprising HfO_2 showing 133 nm optical film thickness; and fifth layer comprising SiO_2 showing 135 nm optical film thickness. And then, said glass substrate was cooled to 80°C; and sixth layer comprising perfluoro methyl silazane showing 10 nm optical film thickness was formed to provide an anti-reflection film.

[0011]
EXAMPLE 2

A BK 7 optical glass substrate with 1.52 refractive index was heated to 250°C; and following layers were successfully formed on this through use of a vacuum vapor deposition device: first layer comprising SiO_2 showing 275 nm optical film thickness; second layer comprising Ta_2O_5 showing 50 nm optical layer thickness; third layer comprising SiO_2 showing 40 nm optical film thickness; fourth layer comprising Ta_2O_5 showing 133 nm optical film thickness; and fifth layer comprising SiO_2 showing 135 nm optical film thickness. And then, said glass substrate was cooled to 80°C; and sixth layer comprising perfluoro methyl silazane showing 10 nm optical film thickness was formed to provide an anti-reflection film.

[0012]
COMPARATIVE EXAMPLE 1

A BK7 optical glass substrate with 1.52 refractive index was heated to 250°C; and following layers were successfully formed on this through use of a vacuum vapor deposition device to form an anti-reflection film: first layer comprising Al_2O_2 showing 138 nm optical film thickness; second layer comprising ZrO_2 showing 275 nm optical film thickness; and third layer comprising MgF_2 showing 138 nm optical film thickness.

[0013]
COMPARATIVE EXAMPLE 2

A BK7 optical glass substrate with 1.52 refractive index was heated to 250°C; and following layers were successfully formed on this through use of a vacuum vapor deposition device: first layer comprising Al_2O_3 showing 138 nm optical film thickness; second layer comprising ZrO_2 showing 275 nm optical film thickness; and third layer comprising MgF_2 showing 138 nm optical film thickness. And then, said glass substrate was cooled to 80°C, and fourth layer comprising perfluoro methyl silazane showing 10 nm optical density thickness was formed on the third layer to provide an anti-reflection film.

[0014]
COMPARATIVE EXAMPLE 3

A BK7 optical glass substrate with 1.52 refractive index was heated to 250°C; and following layers were successfully formed on this through use of a vacuum vapor deposition device to provide an anti-reflection film: first layer comprising SiO_2 showing 275 nm optical film thickness; second layer comprising HfO_2 showing 50 nm optical film thickness; third layer comprising SiO_2 showing 40 nm optical film thickness; fourth layer comprising HfO_2 showing 133 nm optical film thickness; and fifth layer comprising SiO_2 showing 135 nm optical film thickness.

[0015]
Spectral reflectively characteristics of anti-reflection films prepared through examples 1 and 2, comparative example 1 are illustrated in the Figures 1,2,, and 3. As it is clear from these Figures, all anti-reflection films show 5^{o} incidental spectral reflectively characteristics of at most 0.5% reflectively at 150 to 290 nm wavelength width centered at 550 nm designed wavelength.

[0016]
Moisture resistance test
Water droplets comprising pure water were formed on each anti-reflection film prepared through above-explained examples and comparative example; and after they were left undisturbed for 14 hours at $65^{o}C$, 95% relative humidity atmosphere, exterior appearance of each film plane was absorbed. Then, the film plane was wiped with alcohol to evaluate exterior appearance of the film plane. Exterior appearance was evaluated based on standards explained below, and results are shown in the Table 1.

[0017]
Exterior appearance after evaporation of water droplets:
x: large flow marking remaining
o: small flow marking remaining

Exterior appearance after wiping with alcohol
x: no change
△: hardly any flow marking observed
o: no flow marking observed

[0018]
[Table 1]

	after evaporation of water droplets	after wiping with alcohol
example 1	o	o
example 1	o	o
comparative example 1	x	x
comparative example 2	o	△
comparative example 3	o	△

[0019]
As it may be noted from the Table 1, this invention's anti-reflection film to which anti-reflection characteristics were provided through combination of HfO_2 or Ta_2O_5 that is a high refractive index material showing excellent moisture resistance, and SiO_2 that is a low refractive index material showing excellent moisture resistance, and water repelling property was provided through use of most outer layer comprising perfluoro alkyl silazane showed significantly improved moisture resistance in comparison with that of conventional anti-reflection films.

[0020]
[Effects of this invention]
This invention's anti-reflection film shows high anti-reflection effect as well as excellent moisture resistance with at most 0.5% reflectively at 150 nm wavelength width centered at 550 nm designed wavelength; and therefore, it is best suited as anti-reflection film for optical parts which are used in high humidity atmosphere.

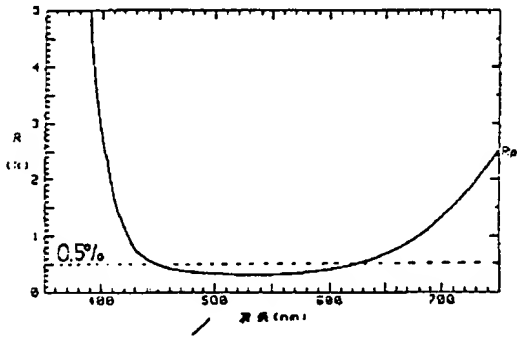
[BRIEF EXPLANATION OF THE FIGURES]
[Figure 1]
It illustrates spectral reflectively characteristics of anti-reflection film prepared in the example 1.

[Figure 2]
It illustrates spectral reflectively characteristics of anti-reflection film prepared in the example 2.

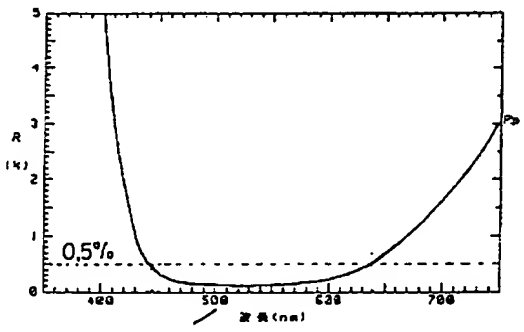
[Figure 3]
It illustrates spectral reflectively characteristics of anti-reflection film prepared in the comparative example 1.

Figures 1 through 3
1: wavelength (nm)

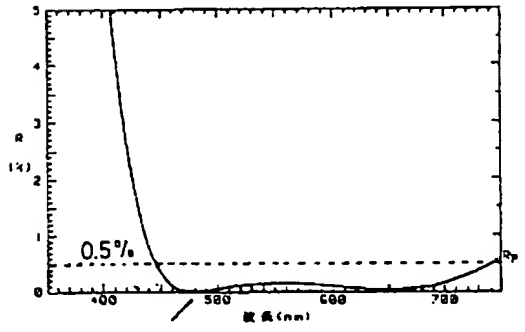
【図1】



【図2】



【図3】



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Translation by: Mie N. Arntson, 512-331-7167

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(71)出願人　000000527
旭光学工業株式会社
東京都板橋区前野町２丁目36番９号

(72)発明者　藤井　秀雄
東京都板橋区前野町２丁目36番９号　旭光学工業株式会社内

(72)発明者　荒木　清
東京都板橋区前野町２丁目36番９号　旭光学工業株式会社内

(74)代理人　弁理士　三浦　邦夫

(54)【発明の名称】　耐湿反射防止膜

(57)【要約】

【目的】　高湿度雰囲気に曝されて表面に水滴が生じた後に蒸発して残ったフローマークを簡単に拭き取ることができる反射防止膜を提供すること。

【構成】　光学ガラス基板上に、設計波長５５０ｎｍで光学膜厚２３４～３１６ｎｍのＳｉO_2 から成る第一層、光学膜厚４３～５８ｎｍのＨｆO_2 又はＴａ$_2$ O_5 から成る第二層、光学膜厚３４～４６ｎｍのＳｉO_2 から成る第三層、光学膜厚１１３～１５３ｎｍのＨｆO_2 又はＴａ$_2$ O_5 から成る第四層、光学膜厚１１５～１５５ｎｍのＳｉO_2 から成る第五層及び光学膜厚５～１５ｎｍのパーフルオロアルキルシラザンから成る第六層を順次形成して構成されたことを特徴とする耐湿反射防止膜である。

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【特許請求の範囲】

【請求項1】　光学ガラス基板上に、設計波長５５０ｎｍで光学膜厚２３４～３１６ｎｍのＳｉO_2 から成る第一層、光学膜厚４３～５８ｎｍのＨｆO_2 又はＴａ$_2$ Ｏ$_5$ から成る第二層、光学膜厚３４～４６ｎｍのＳｉO_2 から成る第三層、光学膜厚１１３～１５３ｎｍのＨｆＯ$_2$ 又はＴａ$_2$ Ｏ$_5$ から成る第四層、光学膜厚１１５～１５５ｎｍのＳｉO_2 から成る第五層及び光学膜厚５～１５ｎｍのパーフルオロアルキルシラザンから成る第六層を順次形成して構成されたことを特徴とする耐湿反射防止膜。

【請求項2】　パーフルオロアルキルシラザンのアルキル基が、炭素数１～４のアルキル基である請求項１記載の耐湿反射防止膜。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、光学機器を構成するレンズ、プリズム等の光学部品、特に高湿度雰囲気で用いられる光学部品に好適な反射防止膜に関する。

【０００２】

【従来技術及びその問題点】従来、光学機器を構成するレンズ、プリズム等の光学部品に用いられる反射防止膜としては、例えば、光学膜厚１３８ｎｍのＡｌ$_2$ Ｏ$_3$ から成る第一層、光学膜厚２７５ｎｍのＺｒO_2 から成る第二層、光学膜厚１３８ｎｍのＭｇF_2 から成る第三層をＢＫ７光学ガラス基板（屈折率＝１．５２）上に順次形成した反射防止膜を使用していた。しかしながら、このような従来の反射防止膜は、その表面に水滴が生じるような高湿度雰囲気では、水滴が長時間かけて蒸発した場合に水滴が存在した部分に白い曇り状のフローマークが残り、このフローマークはアルコール等の溶剤で拭き取っても簡単には落ちないという問題点があった。

【０００３】

【発明の目的】本発明は、上記の従来技術の問題点を解消し、高湿度雰囲気に曝されて表面に水滴が生じた後に蒸発して残ったフローマークを簡単に拭き取ることができる反射防止膜を提供することを目的とする。

【０００４】

【発明の概要】本発明は、耐湿性の高い高屈折率材料であるＨｆO_2 又はＴａ$_2$ Ｏ$_5$ と耐湿性に優れた低屈折率材料であるＳｉO_2 とを組み合わせて反射防止膜を構成し、さらに最外層上に撥水性の高分子材料であるパーフルオロアルキルシラザンから成る層を形成することにより上記目的を達成したものである。

【０００５】すなわち、本発明の耐湿反射防止膜は、光学ガラス基板上に、設計波長５５０ｎｍで光学膜厚２３４～３１６ｎｍのＳｉO_2 から成る第一層、光学膜厚４３～５８ｎｍのＨｆO_2 又はＴａ$_2$ Ｏ$_5$ から成る第二層、光学膜厚３４～４６ｎｍのＳｉO_2 から成る第三層、光学膜厚１１３～１５３ｎｍのＨｆO_2 又はＴａ$_2$ Ｏ$_5$ から成る第四層、光学膜厚１１５～１５５ｎｍのＳｉO_2 から成る第五層及び光学膜厚５～１５ｎｍのパーフルオロアルキルシラザンから成る第六層を順次形成して構成されたことを特徴とする。

【０００６】本発明の反射防止膜において、第六層を構成するパーフルオロアルキルシラザンとしては、充分な撥水性と成膜性を有するものであれば、特に制限はないが、アルキル基の炭素数が１～４のものが好ましい。具体的には、パーフルオロメチルシラザンやパーフルオロジエチルシラザンなどが挙げられる。

【０００７】上記のように、耐湿性の高い高屈折率材料であるＨｆO_2 又はＴａ$_2$ Ｏ$_5$ と耐湿性に優れた低屈折率材料であるＳｉO_2 とを用いて５層からなる反射防止膜を形成し、さらに高湿度雰囲気に曝されても反射防止膜表面に水滴が生じにくいように撥水性を有するパーフルオロアルキルシラザンから成る第六層を最外層に形成することによって優れた耐湿性を有する反射防止膜が得られる。

【０００８】本発明の反射防止膜を構成する各層は、真空蒸着法、スパッタリング法、イオンプレーティング法、イオンビームアシスト法など、任意の方法で形成することができる。

【０００９】

【実施例】次に、実施例に基づいて本発明をさらに詳細に説明するが、本発明はこれによって制限されるものではない。

【００１０】実施例１

屈折率１．５２のＢＫ７光学ガラス基板を２５０℃に加熱し、真空蒸着装置により光学膜厚２７５ｎｍのＳｉO_2 から成る第一層、光学膜厚５０ｎｍのＨｆO_2 から成る第二層、光学膜厚４０ｎｍのＳｉO_2 から成る第三層、光学膜厚１３３ｎｍのＨｆO_2 から成る第四層、光学膜厚１３５ｎｍのＳｉO_2 から成る第五層を順次形成した後、該ガラス基板を８０℃まで冷却し、光学膜厚１０ｎｍのパーフルオロメチルシラザンから成る第六層を形成して反射防止膜を作製した。

【００１１】実施例２

屈折率１．５２のＢＫ７光学ガラス基板を２５０℃に加熱し、真空蒸着装置により光学膜厚２７５ｎｍのＳｉO_2 から成る第一層、光学膜厚５０ｎｍのＴａ$_2$Ｏ$_5$ から成る第二層、光学膜厚４０ｎｍのＳｉO_2 から成る第三層、光学膜厚１３３ｎｍのＴａ$_2$ Ｏ$_5$ から成る第四層、光学膜厚１３５ｎｍのＳｉO_2 から成る第五層を形成した後、該ガラス基板を８０℃まで冷却し、光学膜厚１０ｎｍのパーフルオロメチルシラザンから成る第六層を順次形成して反射防止膜を作製した。

【００１２】比較例１

屈折率１．５２のＢＫ７光学ガラス基板を２５０℃に加熱し、真空蒸着装置により光学膜厚１３８ｎｍのＡｌ$_2$ Ｏ$_3$ から成る第一層、光学膜厚２７５ｎｍのＺｒO_2 か

ら成る第二層、光学膜厚１３８ｎｍのＭｇＦ$_2$ から成る第三層を順次形成して反射防止膜を作製した。

【００１３】比較例２

屈折率１．５２のＢＫ７光学ガラス基板を２５０℃に加熱し、真空蒸着装置により光学膜厚１３８ｎｍのＡｌ$_2$Ｏ$_3$ から成る第一層、光学膜厚２７５ｎｍのＺｒＯ$_2$ から成る第二層、光学膜厚１３８ｎｍのＭｇＦ$_2$ から成る第三層を順次形成した後、該ガラス基板を８０℃まで冷却し、第三層上に光学膜厚１０ｎｍのパーフルオロメチルシラザンから成る第四層を形成して反射防止膜を作製した。

【００１４】比較例３

屈折率１．５２のＢＫ７光学ガラス基板を２５０℃に加熱し、真空蒸着装置により光学膜厚２７５ｎｍのＳｉＯ$_2$ から成る第一層、光学膜厚５０ｎｍのＨｆＯ$_2$ から成る第二層、光学膜厚４０ｎｍのＳｉＯ$_2$ から成る第三層、光学膜厚１３３ｎｍのＨｆＯ$_2$ から成る第四層、光学膜厚１３５ｎｍのＳｉＯ$_2$ から成る第五層を順次形成して反射防止膜を作製した。

【００１５】実施例１、実施例２及び比較例１で得られた反射防止膜の分光反射率特性をそれぞれ図１、図２及び図３に示す。これらの図から明らかなとおり、反射防止膜は、いずれも設計波長５５０ｎｍを中心に波長幅１５０～２９０ｎｍで反射率０．５％以下という５°入射分光反射率特性を示している。

【００１６】耐湿試験

上記の実施例及び比較例で得た各反射防止膜上に純水から成る水滴を載せ、温度６５℃、相対湿度９５％の雰囲気中に１４時間放置した後、その膜面の外観を観察した。次いで、その膜面をアルコールで拭き取り、膜面の外観を評価した。外観は、下記の基準で評価し、結果を表１に示す。

【００１７】水滴蒸発後の外観

×：大きなフローマークが残る。

○：小さなフローマークが残る。

アルコール拭き取り後の外観

×：変化なし。

△：フローマークが殆ど見えない。

○：フローマークは見えない。

【００１８】

【表１】

	水滴蒸発後	アルコール拭き取り後
実施例１	○	○
実施例２	○	○
比較例１	×	×
比較例２	○	△
比較例３	○	△

【００１９】表１から判るように、耐湿性に優れた高屈折率材料であるＨｆＯ$_2$ 又はＴａ$_2$Ｏ$_5$ と耐湿性に優れた低屈折率材料であるＳｉＯ$_2$ とを組み合わせて反射防止特性を付与し、さらにパーフルオロアルキルシラザンから成る最外層を用いた撥水性を付与した本発明の反射防止膜は、従来の反射防止膜に比べて著しく耐湿性が向上している。

【００２０】

【発明の効果】本発明の反射防止膜は、設計波長５５０ｎｍを中心に波長幅１５０ｎｍで反射率０．５％以下の、高い反射防止効果を示すと共に優れた耐湿効果を有しているので、高湿度雰囲気で用いられる光学部品への反射防止膜に最適である。

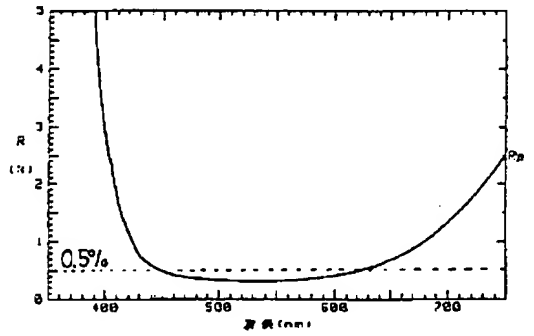
【図面の簡単な説明】

【図１】実施例１で作製した反射防止膜の分光反射率特性図である。

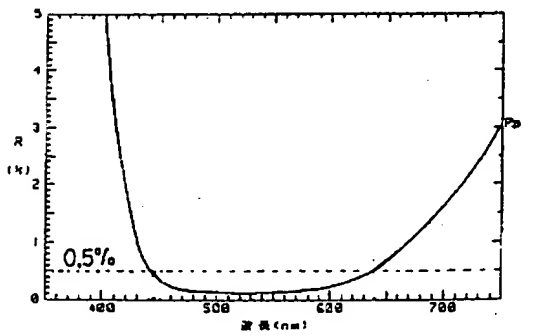
【図２】実施例２で作製した反射防止膜の分光反射率特性図である。

【図３】比較例１で作製した反射防止膜の分光反射率特性図である。

【図１】



【図２】



【図３】